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THE PRODUCTION AND SPECTROSCOPY OF MOLECULAR IONS ISOLATED IN SOLID NEON

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I. INTRODUCTION

Although the mass spectrometric detection of molecular ions is commonplace, relatively little is known about their structures and the properties of their chemical bonds. Studies of the vibrational and electronic

spectra of these species are exceptionally well suited to obtaining this information. Such studies would have the bonus of providing a basis for the development of non-intrusive, *in situ* laser probes for molecular ions in the lower ionosphere and in such important chemical reaction systems as those of chemical vapor deposition and microcircuit etching. Because of their great chemical reactivity, it has been difficult to maintain sufficiently high ion concentrations for molecular spectroscopic study. Despite this difficulty, a survey of the compilation of the spectra of diatomic molecules by Huber and Herzberg [1] reveals the availability of spectroscopic data for a considerable number of diatomic ions. Spectral data have been derived from the analysis of the emission spectra of a few simple polyatomic molecular ions, including CO_2^+ , OCS^+ , CS_2^+ , and N_2O^+ . The recent development of molecular beam techniques and tunable lasers has considerably enhanced our ability to study individual bands at high resolution. Heretofore, studies of a few heavy-atom species, including CF_2 and CF_3 , of such molecular anions as NH_2^- , FHF^- , and ClHCl^- , of several protonated molecules, including H_3^+ , H_3O^+ , HCO^+ , HN_2^+ , and HCNH^+ , and of a number of substituted acetylene and benzene cations have been reported [2-4]. In addition, a substantial body of spectroscopic data, typically at very low resolution, for polyatomic cations can be derived from the photoelectron spectra of the parent species [4].

Matrix isolation studies, in which the ionic species are trapped in dilute solid solution in a rare gas or other inert, rigid matrix material, have provided a valuable adjunct to gas-phase studies of the spectra of molecular ions [5-7]. Under the conditions of the matrix studies, it is possible to store a sufficient concentration of ionic species for a broad spectral survey. A number of ion production techniques have been useful. Charge transfer with an alkali metal has been used to stabilize such species as C_2^- , O_2^- , NO_2^- , O_3^- , and CO_2^- , and the bihalides (XHY^-). Photoionization and chemiionization have led to the stabilization of a number of halomethyl and halomethane cations and anions, as well as of haloacetylene and halobenzene cations. Matrix isolation studies have provided the only spectroscopic data for the HAr_2^+ and HKr_2^+ protonated complexes, as well as for the O_4^- and $\text{O}_2\text{C}\cdots\text{OCO}^-$ cluster anions, stabilized in the presence of alkali metal cations. These latter species are of particular interest, since at the pressures of typical chemical processes ion-molecule reaction to form clusters bound by energies large compared to those of van der Waals complexes is exceedingly common, yet very little is known about the chemical bonding properties of cluster ions. The following discussion will be focused on recent developments in matrix isolation spectroscopy which have extended the range of energies available for ion production and

have yielded new molecular spectroscopic data for a number of molecular ions and dimer ions without the need for an alkali metal to facilitate anion stabilization.

II. PROPERTIES OF RARE GAS MATRICES

Several properties of rare gas matrices are especially important to the stabilization and spectroscopic study of molecular ions and other highly reactive species in the matrix environment. Experience with a wide variety of systems is consistent with the generalization that molecules cannot diffuse through argon at 14 K or neon at 4 K. On the other hand, limited atomic diffusion does occur under these conditions. The extent of this atomic diffusion is dependent on the atomic mass; H-atom diffusion occurs most readily. Rare-gas matrix shifts of both vibrational [8] and non-Rydberg electronic [9] transitions are usually small, with neon the least perturbing matrix material. In order to avoid electrostatic repulsion of ions from the surface of the matrix deposit, overall charge neutrality of the sample is required. Charge transfer interaction may enhance the stability of ion pairs in matrices. Important factors are summarized by the charge transfer equation

$$\Delta E = I.P. - E.A. - e^2/\epsilon R,$$

in which ΔE is the energy difference between the ion pair and the uncharged atom-molecule pair, I.P. is the ionization potential of the electron donor (*i.e.*, the alkali metal), E.A. is the electron affinity of the electron acceptor, and the final term is the Coulombic stabilization energy of the ion pair at the cation-anion separation R . In the gas phase and in photoionization matrix experiments, both the ionization potential of the cation source and R are large, implying that ion-pair stabilization by charge transfer interaction should be negligible. On the other hand, in matrix studies in which an alkali metal atom is used as an electron donor, both the low electron affinity of the alkali metal and the ability of the alkali metal atomic ion to diffuse to a site near the molecular anion, resulting in a large Coulombic term, should enhance the stability of the anion. The price for this anion stabilization is perturbation of the molecular energy levels of the anion by the nearby alkali metal cation.

III. DISCHARGE SAMPLING CONFIGURATION

The codeposition of an Ar:XY sample with a beam of argon atoms that has been excited in a microwave discharge has been a very useful

technique for the production of free radicals and molecular ions in matrix isolation experiments [5-7]. In these experiments, both photoionization of the molecule XY by argon resonance radiation and chemiionization of XY by collision with metastable argon atoms in the region between the end of the discharge tube and the cryogenic observation surface or on the surface of the deposit can occur. The energy range effective for ionization in these experiments is 11.5-11.8 eV; there is very little evidence for significant contributions from higher excited energy levels of argon. Because many important molecules containing only the elements C, H, O, and N have ionization potentials which exceed 11.8 eV, the applicability of this system for ion production is rather severely limited.

Since virtually all molecules have first ionization potentials below about 16 eV, this limitation can be removed by substituting excited neon atoms, which have their first excited energy levels between 16.6 and 16.8 eV, as the energy source for ionization. Pioneering experiments by Knight and co-workers [10] have demonstrated that when this ionization source is used a considerable number of cations and dimer cations can be stabilized in a neon matrix in concentrations sufficient for observation of their electron spin resonance (ESR) spectra. However, the sensitivity of detection of infrared and ultraviolet absorption spectra is considerably lower than that of ESR spectra. Several years ago, Jacox [11] tested the possible application of a beam of excited neon atoms as an ionization source for infrared studies by codepositing an Ar:CF₃NNCF₃ sample with a beam of excited neon atoms. In the corresponding experiments on this system using excited argon atoms, an extremely high yield of CF₃ free radicals was obtained, together with a small yield of CF₃⁺, formed by secondary photoionization of CF₃, a process which is substantially inhibited by the Franck-Condon effect. When excited neon atoms were substituted, only a very small yield of CF₃ resulted, yet the yield of CF₃⁺ was somewhat enhanced. This result indicated that the process which leads to ion production in the excited neon atom experiments must differ significantly from that in the excited argon atom experiments. The appearance of CF₃⁺ also suggested that ions might also be stabilized in detectable concentrations in other systems.

Further tests of the use of excited neon atoms as an ionization source for infrared studies were performed using the sampling configuration shown in Figure 1. Neon atoms passing through a Vycor or quartz discharge tube were excited by 50 to 80 W of 2450 MHz microwave power. The pinhole, with a diameter of approximately 1 mm, aids in the maintenance of a sufficient pressure for satisfactory coupling of the discharge and inhibits backstreaming of the molecule XY into the discharge region.

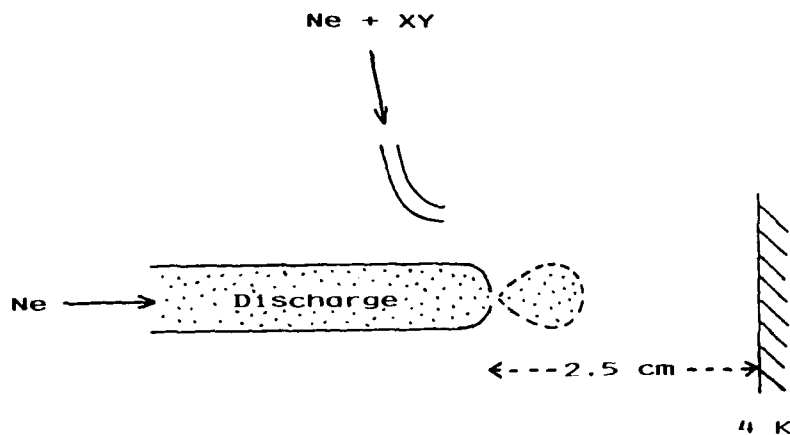


Figure 1. Sampling configuration used in matrix isolation studies of the products of the interaction of discharge-excited neon atoms with the molecule XY (CO_2 , O_2 , N_2 , CO).

The species XY interacts with excited neon atoms and their resonance radiation over a path length of approximately 2.5 cm before being frozen onto the cryogenic observation surface, maintained at a temperature of approximately 5 K by using a continuous transfer liquid helium cell. At mole ratios typical of these experiments, a molecular ion formed in this 2.5 cm mixing region can experience at most two or three collisions before reaching the low-temperature surface. Because ion-molecule reactions occur very efficiently, at the Ne:XY mole ratios of 100 to 400 used in most of these experiments there is a significant probability for the formation of dimer cations and anions. The use of a neon matrix eliminates the possibility of energy degradation by a matrix material with lower excited energy levels and provides for minimal perturbation of the ion energy levels by the matrix. The exceptionally high sensitivity of the Fourier transform infrared detection system used in these experiments [12], operated at a resolution of 0.2 cm^{-1} , has greatly facilitated ion detection in these studies.

IV. IONS PRODUCED FROM CO_2

A. CO_2^+

Because the ionization potential of CO_2 is 13.77 eV [13], substantially above the energy accessible using excited argon atoms, and because the

gas-phase band center of the antisymmetric stretching fundamental, ν_3 , of CO_2^+ has been determined by Kawaguchi and co-workers [14] to lie at 1423.08 cm^{-1} , CO_2 was chosen as the test molecule for the first studies with the new apparatus. As is shown in trace (a) of Figure 2, a structured

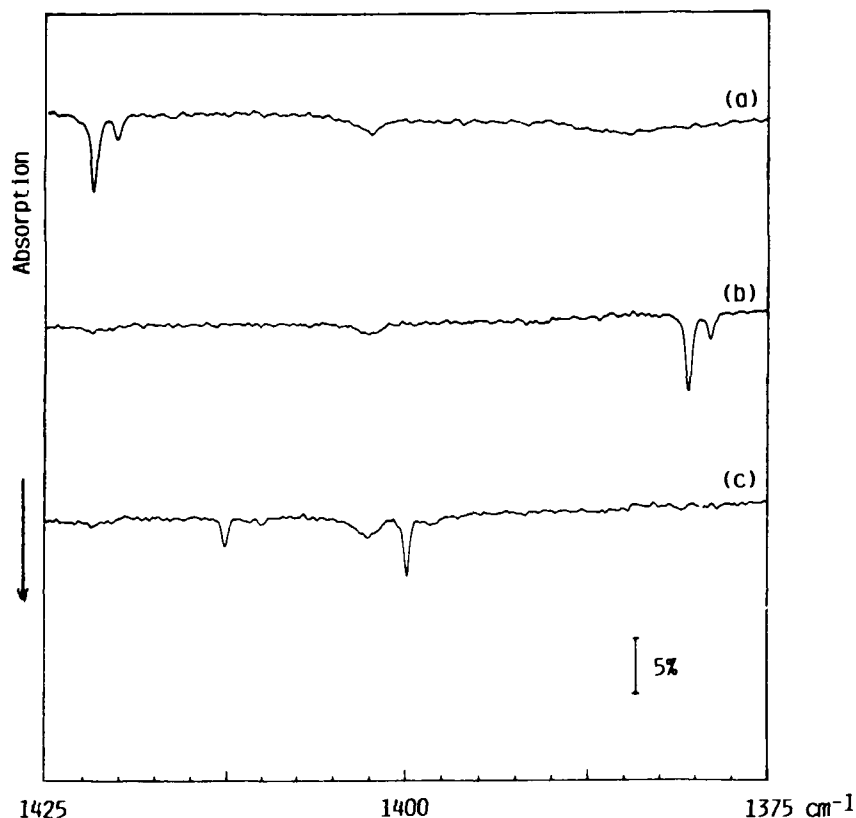


Figure 2. (a) 3.21 mmol Ne: CO_2 = 400 codeposited over period of 176 min with 3.96 mmol discharged Ne. (b) 3.21 mmol Ne: CO_2 (90% ^{13}C) = 400 codeposited over period of 179 min with 3.74 mmol discharged Ne. (c) 5.78 mmol Ne: CO_2 (91.5% ^{18}O) = 500 codeposited over period of 219 min with 4.71 mmol discharged Ne.

absorption appeared at 1421.7 cm^{-1} , only 1.4 cm^{-1} from the gas-phase band center of ν_3 of CO_2^+ . Furthermore, as is shown in traces (b) and (c) of Figure 2, there was a substantial shift in the position of this absorption when a CO_2 sample which was highly enriched in $^{13}\text{CO}_2$ was substituted,

and there were two new lower frequency peaks with similar contours when a CO_2 sample enriched to 91.5% in oxygen-18 was used. Additional details of these observations are given in a forthcoming publication [15]. When the observed frequencies for the four isotopic products were subjected to a least-squares force constant fit to a vibrational potential appropriate for linear CO_2^+ , the average frequency error was 0.2 cm^{-1} and the largest deviation was 0.5 cm^{-1} , strongly supporting the assignment of the 1421.7 cm^{-1} absorption to ν_3 of CO_2^+ .

In each of the spectra shown in Figure 2, there was a broad absorption at 1402.4 cm^{-1} , close to the 1408.4 cm^{-1} band center of the ground-state bending fundamental, ν_2 , of gas-phase H_2O^+ , inferred from the extrapolation of its emission spectrum [16,17] and from the analysis of the high-resolution photoelectron spectrum of H_2O [18]. Since H_2O , which has an ionization potential of 12.61 eV [13], can desorb from the walls of the deposition system in all of the matrix experiments, this absorption is tentatively assigned to ν_2 of H_2O^+ .

B. CO_2^-

Also present in the studies of Ne: CO_2 samples was a prominent, structured absorption at 1658.3 cm^{-1} , which has isotopic behavior appropriate for its assignment to the antisymmetric stretching fundamental, ν_3 , of CO_2^- . This fundamental absorption was first identified at 1671 cm^{-1} by Hisatsune and co-workers [19,20] in studies of the infrared spectra of gamma-irradiated sodium formate pressed in alkali halide disks. The first detection of CO_2^- in a rare-gas matrix was reported by Jacox and Milligan [21], who observed a complicated pattern of absorptions near 1600 cm^{-1} when an Ar: CO_2 sample was codeposited with a beam of alkali metal atoms. More recent matrix isolation studies in several laboratories [22-27] have provided further details on the nature of the alkali metal interaction and have presented evidence for the stabilization of CO_2 dimer anions, as well as of M^+CO_2^- , in this system. A least-squares force constant fit of the isotopic data obtained in the excited neon atom experiments of Jacox and Thompson [15] to the vibrational potential of CO_2^- , assuming a valence angle of 135 degrees, was very satisfactory. The average frequency error was 0.2 cm^{-1} , and the largest deviation was 0.5 cm^{-1} .

There were two important differences between the behavior of the 1658.3 cm^{-1} peak in the excited neon atom studies and that of the absorptions assigned to CO_2^- in the earlier matrix isolation studies. First, there is an upward shift of 50 or 60 cm^{-1} in the CO_2^- absorption in the neon matrix studies. This frequency difference is attributable to differences in

the environment of CO_2^- in the two experimental systems, illustrated in Figure 3. As is shown on the left side of the figure, when an alkali metal, M, is present in the system it can diffuse to a site adjacent to CO_2 , and charge transfer interaction can lead to ion pair formation and stabiliza-

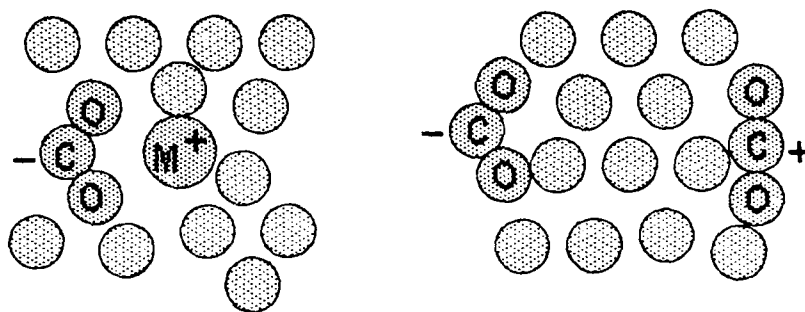


Figure 3. Environment of a typical CO_2^- ion in a matrix isolation experiment in which the alkali metal M is codeposited with CO_2 compared with the environment of a typical CO_2^- ion in an experiment in which photoionization or Penning ionization of CO_2 provides the electron source.

tion. The observed dependence of the CO_2^- absorption pattern on the alkali metal chosen for the experiment provides evidence for the occurrence of substantial ion pair interactions. In the studies of the products of the interaction of lithium atoms with CO_2 [22-25], evidence was obtained for the stabilization of a cyclic Li^+CO_2^- product and of a planar Li^+OCO^- species in the matrix. Only the cyclic structure, illustrated in Figure 3, was identified in the studies of the interaction of the heavier alkali metals with CO_2 [26,27]. In contrast, when photo- or chemiionization of CO_2 occurs, the resulting electron is captured to form the anion. Only a small fraction of the CO_2 is ionized in these experiments, and CO_2^+ , unlike the alkali metal atomic cations, cannot diffuse through solid neon. Thus, as is shown in the right hand portion of Figure 3, most of the CO_2^- will be stabilized in sites separated from CO_2^+ by several intervening neon atoms, the ion field will be relatively homogeneous, and charge transfer stabilization will be minimized. This latter factor accounts for the destruction of the CO_2^- absorption when the sample containing CO_2^+ is exposed for a few minutes to radiation even of wavelength 490 nm and longer, in marked contrast to the persistence and, indeed, the growth in the CO_2^- absorption

on exposure of the samples containing an alkali metal to visible and near ultraviolet radiation.

When a Ne:CO₂ sample containing molecular ions was warmed to approximately 8 K and recooled, the 1658.3 cm⁻¹ absorption diminished in intensity, and a peak at 1665.5 cm⁻¹ grew. This behavior is consistent with the assignment of the 1665.5 cm⁻¹ peak to a CO₂ dimer anion. In several of the earlier matrix studies [22,23,26], absorptions which appeared a few cm⁻¹ above the principal M⁺CO₂⁻ absorption were also attributed to CO₂ adducts. *Ab initio* calculations by Fleischman and Jordan [28] suggest that (CO₂)₂⁻ should have two stable structures. The structure of D_{2d} symmetry is more stable by approximately 0.2 eV than is O₂C··OCO⁻, which has C_s symmetry. Their calculated vibrational frequencies for the less stable C_s structure, with only weak coupling between the CO₂ and the CO₂⁻ moieties, agree well with the observed small shift in ν_3 of CO₂⁻ on formation of the CO₂ adduct, implying either that the C_s structure has the lower energy or that there is a substantial potential barrier to the rearrangement of the initially formed C_s dimer anion to the D_{2d} form.

V. IONS PRODUCED FROM O₂

In some of the studies of the interaction of excited neon atoms with Ne:CO₂ samples, weak absorptions appeared at 1164.4 and 1320.3 cm⁻¹. The intensities of these absorptions were enhanced in experiments in which O₂ was known to be present. Since the ionization potential of O₂ is 12.07 eV [13], it was also a suitable candidate for the excited neon atom experiments. Therefore, a study of the codeposition of a Ne:O₂ sample with a beam of excited neon atoms was conducted. The two unidentified absorptions were prominent, as were the ν_3 absorption of O₃ at 1039.9 cm⁻¹ and an absorption at 973.1 cm⁻¹. A less intense product absorption appeared at 796.3 cm⁻¹ and much weaker absorptions at 2808.5 and 2948.6 cm⁻¹. The peaks near 1164, 1320, 2808, and 2949 cm⁻¹ behaved similarly when the sample was exposed to filtered mercury-arc radiation. The photodecomposition threshold of all four of these peaks was near 420 nm. Although the 973.1 cm⁻¹ peak had a somewhat higher photodecomposition threshold, when the sample was exposed to mercury-arc radiation of wavelength longer than 345 nm, this peak disappeared more rapidly than did the group of four peaks. The 796.3 cm⁻¹ peak disappeared relatively slowly at that stage of the experiment, and the O₃ absorption was unchanged. Thus, the filtered photolysis observations indicate that O₃ and at least three other products are formed in this experimental system.

Isotopic substitution experiments have provided information leading to the positive identification of these new products. Studies using a $\text{Ne}^{16}\text{O}_2\text{:O}_2$ (93% ^{18}O) sample were especially valuable. The 900-1400 cm^{-1} spectral region of a typical sample deposit of this composition is shown in Figure 4. The O_3 absorption at 1039.9 cm^{-1} , which has a

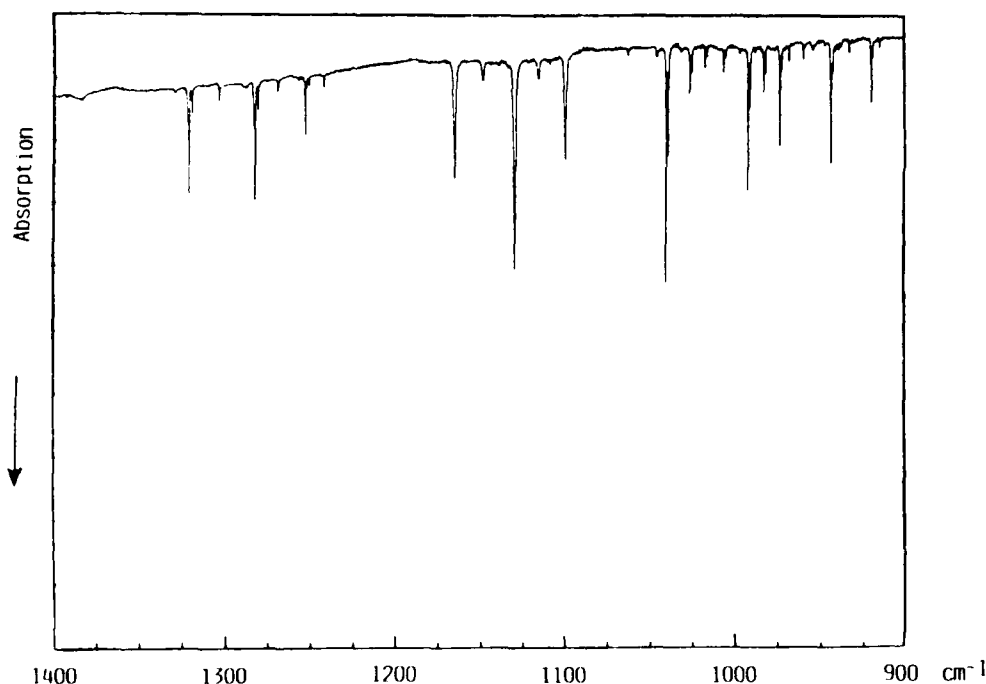


Figure 4. 4.60 mmol $\text{Ne}^{16}\text{O}_2\text{:O}_2$ (93% ^{18}O) = 200:1:1 codeposited over period of 240 min with 6.85 mmol discharged Ne.

partly resolved low frequency component, is the most prominent peak in the spectrum. Peaks are contributed by all five of the other oxygen-isotopic O_3 species, but only that of $^{16}\text{O}^{18}\text{O}^{18}\text{O}$ is prominent. This behavior is consistent with the formation of O_3 by the reaction of ^{16}O atoms formed from trace impurities of H_2O in the discharge with the $^{16}\text{O}_2$ and $^{18}\text{O}_2$ (and with much smaller concentrations of $^{16}\text{O}^{18}\text{O}$) in the sample. Only a small amount of $^{18}\text{O}_3$ was formed by backstreaming of the $\text{Ne}:\text{O}_2$ sample into the discharge region. A similar isotopic substitution pattern was observed for the absorption at 796.3 cm^{-1} , suggesting its assignment to another product which possesses three oxygen atoms. Because of its

close proximity to the absorption near 800 cm^{-1} which was assigned to ν_3 of O_3^- in earlier argon-matrix experiments in which an alkali metal was present [29], its assignment to O_3^- is suggested. The isotopic shifts observed for this peak also correspond with those observed for M^+O_3^- in the earlier experiments, supporting the assignment. Each of the remaining product absorptions is replaced by three absorptions, of which the central one is the most prominent, in this isotopic study. This behavior requires that the products which contribute these absorptions each possess two equivalent O_2 units.

Further information was acquired through studies of the spectra of randomly oxygen-18 substituted samples such as that shown in Figure 5.

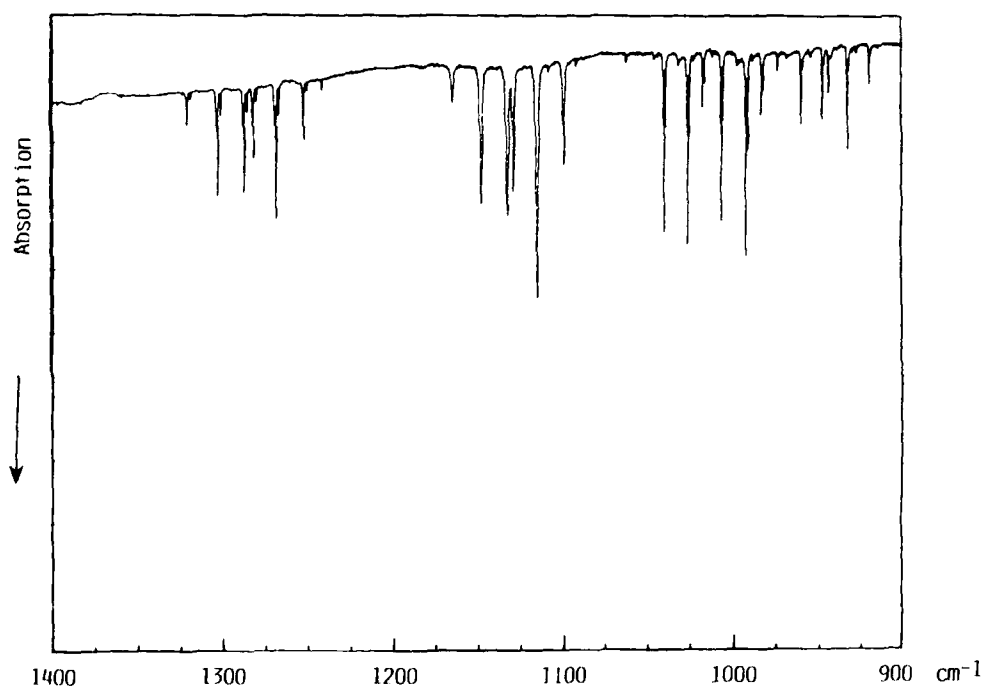


Figure 5. 6.47 mmol $\text{Ne}:\text{O}_2$ (57.8% ^{18}O) = 100 codeposited over period of 287 min with 8.88 mmol discharged Ne.

Each of the product absorptions of the $^{16}\text{O}_2$ studies is replaced by six well resolved peaks. The four isotopic forms of O_3 which have ^{16}O in at least one end position contribute more prominent absorptions than do $^{18}\text{O}^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_3$, consistent with the hypothesis that most of the O_3

results from the reaction of ^{16}O impurity formed in the discharge with isotopically substituted O_2 . A similar intensity pattern is observed for the 796.3 cm^{-1} group of peaks, which have been attributed to O_3^- . For each of the remaining groups of peaks, the absorption contributed by the species which contains only oxygen-16 is relatively weak. It is noteworthy that the isotopic shift and intensity patterns of the 973.1 , 1164.4 , and 1320.3 cm^{-1} groups of absorptions are very similar.

The behavior of the weak absorptions at 2808 and 2946 cm^{-1} on isotopic substitution is shown in the three traces of Figure 6. As is shown in trace (a), each of these two absorptions is replaced by three peaks, with the central peak approximately twice as intense as the outer two peaks,

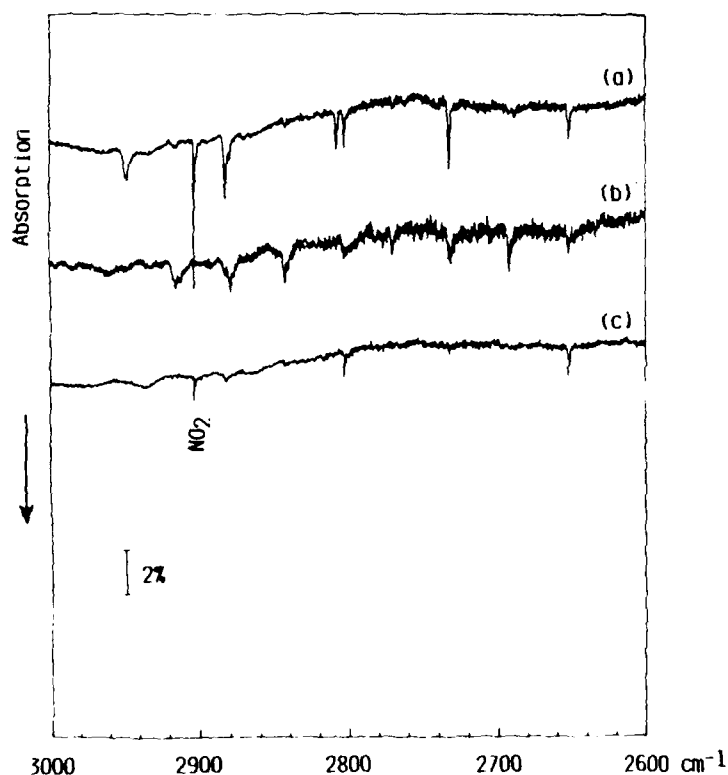


Figure 6. (a) $8.24\text{ mmol Ne:}^{16}\text{O}_2\text{:O}_2\text{ (93\% }^{18}\text{O)} = 200\text{:1:1}$ codeposited over period of 266 min with 8.56 mmol discharged Ne. (b) $5.78\text{ mmol Ne:}^{16}\text{O}_2\text{:O}_2\text{ (57.8\% }^{18}\text{O)} = 100$ codeposited over period of 234 min with 6.85 mmol discharged Ne. (c) $4.39\text{ mmol Ne:O}_2\text{ (93\% }^{18}\text{O)} = 200$ codeposited over period of 190 min with 5.13 mmol discharged Ne.

when a sample having a $\text{Ne}^{16}\text{O}_2^{18}\text{O}_2$ mole ratio of approximately 200:1:1 is used. (The sharp absorption at 2903 cm^{-1} is contributed by NO_2 produced from trace atmospheric impurities in the discharge.) In trace (b), for a $\text{Ne}:\text{O}_2 = 100$ sample with 57.8% random oxygen-18 isotopic substitution, peaks are contributed by other oxygen-isotopic species of the product. As is shown by trace (c), for a $\text{Ne}:\text{O}_2$ (93% ^{18}O) sample, there are no new peaks at frequencies below the 2802.9 and 2651.3 cm^{-1} peaks attributed to the fully oxygen-18 substituted product in the experiment of trace (a).

A. O_4^-

The O_4^- ion was first detected in the mass spectrometric studies of Conway and Nesbitt [30], who found it to be stable by approximately 13.5 kcal/mol with respect to $\text{O}_2 + \text{O}_2^-$. Recent mass spectrometric studies by Hiraoka [31] have revised this stability downward to 10.5 kcal/mol, a value which still greatly exceeds the stability of neutral O_4 , a van der Waals molecule. The chemical bonding properties of O_4^- are of particular interest, since it is formed by the overlap of antibonding orbitals on O_2 and O_2^- . INDO calculations by Conway [32] suggested that a planar *trans*-configuration (C_{2h}) of the four atoms is the most stable structure of O_4^- . Interest in this species is enhanced by mass spectrometric studies [33,34], which have established that it is a key intermediate in the reaction sequence which leads to the appearance of NO_3^- in the D region of the terrestrial ionosphere.

In studies of the codeposition of $\text{Ar}:\text{O}_2$ samples with a beam of alkali metal atoms, Andrews [35,36] observed an absorption near 1000 cm^{-1} which was contributed by a product which possesses two equivalent O_2 units interacting with the alkali metal atom. The assignment of this absorption to an O_2MO_2 species in which the alkali metal atom occupied a central position was suggested. Subsequently, Jacox and Milligan [37] also observed this absorption and showed that, although *trans*- O_4^- has ten isotopic species, there are several near degeneracies. The absorptions which they observed in an $\text{Ar}:\text{O}_2$ (55% ^{18}O) + Cs experiment were in good agreement with the calculated isotopic absorption pattern for ν_5 (b_u) of the *trans*- O_4^- structure proposed by Conway. In Raman spectroscopic studies of this system, Smardzewski and Andrews [38] observed a band near 300 cm^{-1} which could be assigned to the central O··O stretching fundamental of *trans*- O_4^- . Nevertheless, there has been lingering concern regarding the observation of only six oxygen-isotopic absorptions, as well as about the adequacy of the INDO approximation for determining the

structure of O_4^- . Recent *ab initio* calculations by Ohta and Morokuma [39] suggest that O_4^- may possess a distorted "T" structure. However, the calculated stability of 2.8 kcal/mol for this structure is considerably less than the 10.5 kcal/mol value determined by mass spectrometry.

In the excited neon atom studies, the proximity of the 973.1 cm^{-1} absorption to that attributed to *trans*- O_4^- in the alkali metal atom studies, the demonstration that the carrier of this absorption possesses two equivalent O_2 units, and the similar oxygen-isotopic shifts all suggest the assignment of this absorption to O_4^- . Because the observation of two equivalent O_2 units is inconsistent with the distorted "T" structure, the spectroscopic implications of the *trans*- O_4^- structure have been explored in more detail. The normal vibrations of species with a *trans*- O_4 structure are summarized in Table I. A least squares force constant fit to the ob-

TABLE I

Normal vibrations of *trans*- O_4 species.

Symmetry	Mode	Type of Vibration
a_g	ν_1	Symmetric O=O stretch
	ν_2	O···O stretch
	ν_3	Symmetric in-plane bend
a_u	ν_4	Torsion
b_u	ν_5	Antisymmetric O=O stretch
	ν_6	Antisymmetric in-plane bend

served frequencies of the isotopically substituted species which contribute the 973.1 cm^{-1} group of absorptions and to the Raman data reported by Smardzewski and Andrews [38] for the O···O stretching fundamentals of $Cs^{16}O_4$ and $Cs^{18}O_4$ yielded a calculated frequency pattern which was in very good agreement with the observed one. The accidental degeneracies calculated for the two $^{16}O_3^{18}O^-$ species, the three $(^{16}O^{18}O)_2^-$ species, and the two $^{16}O^{18}O_3^-$ species were preserved to within 0.1 cm^{-1} . The average frequency error was 1.0 cm^{-1} , with the largest frequency deviation 1.8 cm^{-1} . The relative intensities calculated for *trans*- O_4 species which have the accidental degeneracies noted above and which would be formed in samples having the oxygen-isotopic composition of the experiments of Figures 4 and 5 are shown by the dark bars of Figures 7 and 8, respectively. Adjacent to the dark bars are the observed integrated intensities observed

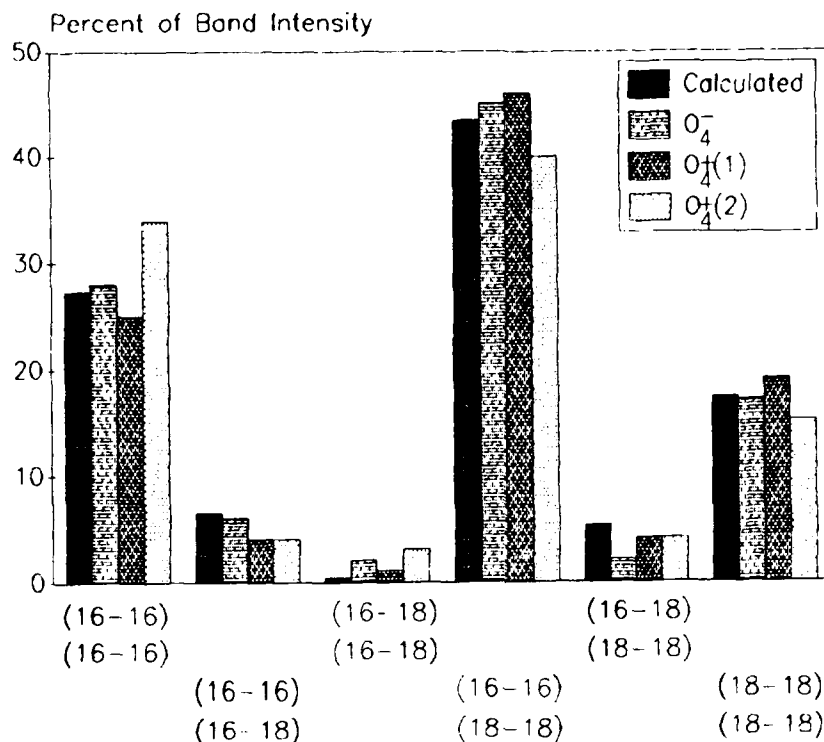


Figure 7. Calculated relative intensities of isotopic components of a *trans*- O_4 species compared with the relative intensities of isotopic components of the absorptions at 973.1 (O_4^-), 1164.4 ($O_4^+(1)$), and 1320.3 ($O_4^+(2)$) cm^{-1} observed in the experiment of Figure 4.

for the absorptions attributed to O_4^- in these two experiments. Considering the uncertainty in the estimation of the baseline for the sharp peaks observed in these experiments, the agreement is very good, supporting the assignment of the 973.1 cm^{-1} absorption to *trans*- O_4^- .

B. O_4^+

The O_4^+ cation was first identified in mass spectrometric studies by Yang and Conway [40]. The INDO calculations of Conway [32] yielded a *trans*- O_4^+ structure with valence angles differing by only a few degrees from those of *trans*- O_4^- . No other calculations of the O_4^+ structure have been published. Hiraoka [31] has recently summarized experimental measurements of the strength of the central O··O bond of O_4^+ , for which he reported a value of 9.2 kcal/mol. Mass spectrometric studies have also

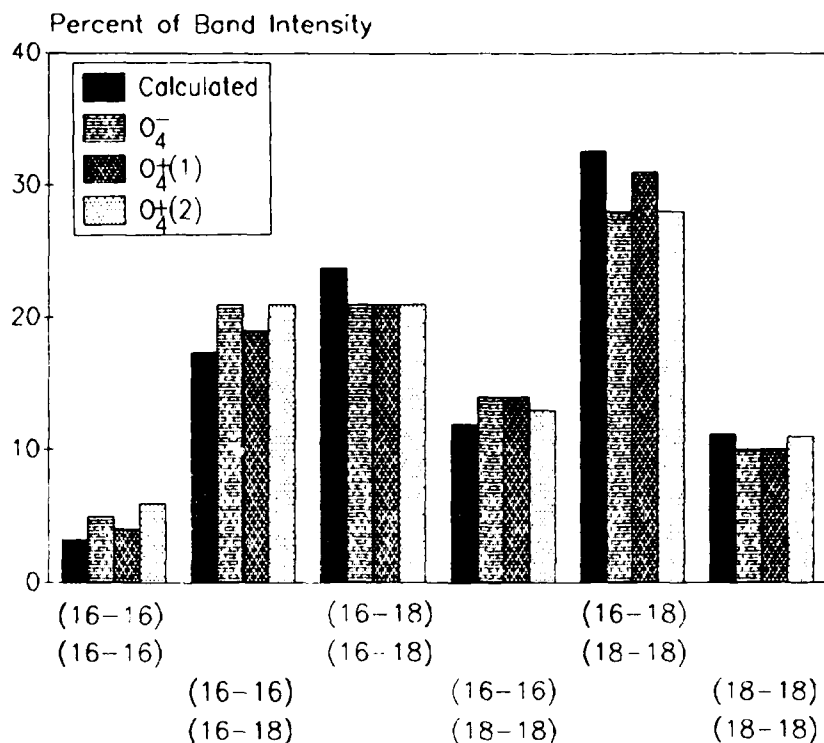


Figure 8. Calculated relative intensities of isotopic components of a *trans*- O_4 species compared with the relative intensities of isotopic components of the absorptions at 973.1 (O_4^-), 1164.4 ($O_4^+(1)$), and 1320.3 ($O_4^+(2)$) cm^{-1} observed in the experiment of Figure 5.

determined that O_4^+ is intermediate in the formation of the protonated water clusters which dominate the ionic species observed in the lower ionosphere. However, no vibrational or electronic spectral data have been reported for O_4^+ .

The expectation that O_2^+ should be formed on codeposition of a Ne: O_2 sample with a beam of excited neon atoms, the prevalence of O_4^+ detection in mass spectrometric studies at moderate oxygen pressures, and the isotopic substitution pattern all suggest that the absorptions at 1164, 1320, 2808, and 2949 cm^{-1} may be contributed by O_4^+ . The results of the experiment shown in Figure 4 require that this species possess two equivalent O_2 units, ruling out many structures which might be proposed for O_4^+ . The isotopic shift and intensity pattern associated with the 1164

cm^{-1} peak is closely similar to that of the 973.1 cm^{-1} absorption, here assigned to ν_5 (b_u) of trans-O_4^- , suggesting that the 1164 cm^{-1} peak may arise from the same fundamental of trans-O_4^+ . The integrated intensities of the isotopic components of this absorption are shown to the right of the corresponding intensities of trans-O_4^- species in Figures 7 and 8. The agreement with the trans-O_4^- intensities and with the calculated intensities is sufficiently good to support the assignment of the 1164 cm^{-1} absorption to trans-O_4^+ . A preliminary least-squares force constant fit to the absorptions assigned to the ν_5 (b_u) fundamental of the isotopically substituted O_4^+ species gave excellent agreement between the observed and calculated frequencies. In agreement with the observations, the absorption of this fundamental of the $^{16}\text{O}^{16}\text{O}^{18}\text{O}^{18}\text{O}^+$ species was calculated to lie somewhat below the mean of the absorptions of the fully oxygen-16 and oxygen-18 substituted cations. The infrared-inactive ν_1 (a_g) fundamental was calculated to have a higher vibrational frequency than ν_5 (b_u), and the ν_1 vibrational frequency of $^{16}\text{O}^{16}\text{O}^{18}\text{O}^{18}\text{O}^+$ was calculated to lie somewhat above the mean of the ν_1 fundamentals of the fully oxygen-16 and oxygen-18 substituted species. The mixed oxygen-isotopic absorption related to the 2808 cm^{-1} absorption in the experiment of Figure 6(a) appeared slightly above the mean of the other two peaks, suggesting the assignment of the 2808 cm^{-1} absorption to the $(\nu_1 + \nu_5)$ combination band of $^{16}\text{O}_4^+$. This assignment locates the ν_1 fundamental of this species at 1644 cm^{-1} . When the values derived for ν_1 of the various isotopic species of trans-O_4^+ were included in the least-squares force constant fit, the average frequency error was 0.5 cm^{-1} . No calculated frequency for ν_5 of an isotopic species deviated from the observed value by more than 0.6 cm^{-1} , and no calculated frequency for ν_1 deviated from a value derived from the combination band frequencies by more than 1.9 cm^{-1} .

The 1320 cm^{-1} absorption has an isotopic shift and intensity (Figures 7 and 8, least shaded bars) pattern which is very similar to that of the 1164 cm^{-1} absorption. Although one might propose that either cis-O_4^+ or a rectangular O_4^+ structure might also be stabilized, each of these two species would have two infrared-active absorptions for $(^{16}\text{O}^{16}\text{O})(^{18}\text{O}^{18}\text{O})^+$ between the 1320 cm^{-1} absorption of $^{16}\text{O}_4^+$ and the 1252 cm^{-1} absorption of $^{18}\text{O}_4^+$. Moreover, detailed calculations demonstrate that these two absorptions should not be accidentally degenerate, but should be shifted by only a few cm^{-1} from the absorptions of the fully oxygen-16 and oxygen-18 substituted species. Because of the weak central O··O bond, all of the vibrational fundamentals of trans-O_4^+ except ν_1 (a_g) and ν_5 (b_u) should lie below about 300 cm^{-1} . Therefore, it is possible that the 1320 cm^{-1} absorption may be contributed by a combination band

involving the ν_5 (b_u) fundamental and one or more low frequency fundamentals of $trans\text{-O}_4^+$ which have an overall a_g symmetry. Alternatively, this absorption may be contributed by a combination band involving a number of low frequency fundamentals with overall b_u symmetry which interacts strongly with ν_5 (b_u). The 151 cm^{-1} separation of the 2949 cm^{-1} peak from the 2808 cm^{-1} peak corresponds sufficiently well with the 156 cm^{-1} separation of the 1320 cm^{-1} peak from the 1164 cm^{-1} peak to suggest that the assignment of the 2949 cm^{-1} peak differs from that of the 1320 cm^{-1} peak by the addition of one quantum of ν_1 (a_g). Further details regarding the vibrational spectra and assignment of O_4^+ and O_4^- will be given in a forthcoming publication [41].

VI. IONS PRODUCED FROM N_2

The first ionization potential of N_2 has been determined [13] to equal 15.58 eV . A number of workers have detected the mass spectrum of N_4^+ . These observations have been summarized by Hiraoka and Nakajima [42], who have recently found N_4^+ to be stable by approximately 23 kcal/mol with respect to $\text{N}_2 + \text{N}_2^+$. *Ab initio* calculations by de Castro and co-workers [43] suggest that N_4^+ should have a linear ground-state structure and that it should be bound by approximately 30 kcal/mol . Knight and co-workers [44] have detected the ESR spectrum of N_4^+ isolated in a neon matrix. Both their analysis of the ESR spectrum and their *ab initio* calculations for this system are consistent with the linear structure obtained in the earlier calculations.

When $\text{Ne:N}_2 = 100$ or 200 samples were codeposited with a beam of excited neon atoms, a very sharp, moderately intense absorption appeared at 2237.6 cm^{-1} , intermediate between the positions of the vibrational fundamentals of ground-state N_2 (2329.9 cm^{-1}) and N_2^+ (2174.8 cm^{-1}) [1]. The threshold for the photodestruction of this new peak was near 420 nm , but there were no other photolyzable product absorptions.

The position of this new absorption and its photolytic instability suggested its assignment to N_4^+ , which was tested by isotopic substitution studies. In experiments on a $\text{Ne:}^{14}\text{N}_2\text{:}^{15}\text{N}_2 = 200:1:1$ sample, the most prominent photolyzable product absorptions appeared at 2237.6 , 2178.9 , and 2163.2 cm^{-1} , with the intensity of the 2178.9 cm^{-1} peak approximately 1.3 times that of the other two peaks. In addition, a less intense photolyzable product absorption appeared at 2266.0 cm^{-1} .

The infrared-active ν_3 (Σ_u^+) fundamental of linear N_4^+ is symmetrically separable from all other vibrations of this molecule, making an estimate of the stretching force constant for the end nitrogen-nitrogen

bonds especially simple. However, most of the partially nitrogen-15 substituted N_4^+ species, including $^{14}N^{14}N^{15}N^{15}N^+$, have a lower symmetry, with all three stretching vibrations in the Σ^+ symmetry block. When the preliminary value (20.64×10^2 N/m) of the end nitrogen-nitrogen stretching force constant and an estimated value of 2×10^2 N/m for the central N-N stretching force constant were used in the 3×3 calculation of the stretching fundamentals of the isotopic species of N_4^+ , a value of 2293.6 cm^{-1} was obtained for $\nu_1 (\Sigma_g^+)$ of $^{14}N_4^+$. The calculated position of the $\nu_3 (\Sigma_u^+)$ absorption of $^{15}N_4^+$ was 2161.8 cm^{-1} , in very good agreement with the observed value. In this simple approximation the calculated positions of the two high frequency stretching absorptions of $^{14}N^{14}N^{15}N^{15}N^+$ are 2274.4 and 2180.1 cm^{-1} . The agreement with the observed absorptions at 2266.0 and 2178.9 cm^{-1} is sufficiently good to suggest that both of these absorptions are contributed by this asymmetrically substituted N_4^+ species. Because the two absorptions are relatively close to one another, intensity sharing should occur, explaining the observed intensity ratio of approximately 1:1.3:1 for the peaks at 2237.6 , 2178.9 , and 2163.2 cm^{-1} in the $Ne:^{14}N_2:^{15}N_2 = 200:1:1$ study, which differs significantly from the expected 1:2:1 ratio.

Other experiments were conducted on $Ne:N_2$ samples with random nitrogen-15 enrichment up to about 50% and on $Ne:^{15}N_2$ samples. In these experiments, very weak absorptions assigned to ν_1 of $^{14}N^{14}N^{15}N^{14}N^+$ and $^{14}N_3^{15}N^+$ were identified at 2270.0 and 2271.1 cm^{-1} , respectively. A least-squares fit of the two stretching force constants to the observed isotopic frequencies for linear N_4^+ gave calculated frequencies with an average deviation from the observed values of 0.3 cm^{-1} and with no deviation greater than 0.8 cm^{-1} , supporting the assignment of these absorptions to ν_1 of N_4^+ . The position of $\nu_1 (\Sigma_g^+)$ of $^{14}N_4^+$ obtained in this more refined calculation was 2282.6 cm^{-1} .

No infrared absorption attributable to an anion species was observed in the $Ne:N_2$ experiments. The ionization potential of N_2^- is -1.9 eV , but there is some evidence for the existence of vibrational structure for ground-state N_2^- [1]. The detection of N_4^- has not been reported. Therefore, it is likely that charge neutrality is preserved in these experiments by the stabilization of small concentrations of such species as O_2^- , which is infrared inactive, and OH^- .

VII. IONS PRODUCED FROM CO

The first ionization potential of CO is 14.014 eV , and the second ionization potential, to form $CO^+ A \ ^2\Pi_{1/2}$, is 16.55 eV [13,45], in near

coincidence with the first excited energy level (16.6 eV) of neon atoms. Therefore, the formation of CO^+ under the conditions of these experiments is energetically feasible. The ESR spectrum of CO^+ in this system has been reported by Knight and Steadman [46,47]. The $\Delta G_{1/2}$ value (i.e., vibrational fundamental frequency) for ground-state CO^+ in the gas phase is 2183.9 cm^{-1} [1], sufficiently close to a weak, photosensitive absorption observed at 2194.5 cm^{-1} in Ne:CO samples codeposited with a beam of excited neon atoms to suggest the assignment of this matrix absorption to CO^+ .

The CO dimer cation, $\text{OC}\cdots\text{CO}^+$, is known to be quite strongly bound. Its C \cdots C bond dissociation energy was estimated to be 22.4 ± 0.9 kcal/mol in a recent molecular beam photoionization study [48], but theoretical studies [49] suggest that the value may be substantially greater. The ESR spectrum of $(\text{CO})_2^+$ was reported by Knight and co-workers [50] in neon matrix experiments using sampling conditions very similar to those of the present experiments. These workers also performed *ab initio* calculations which indicated that ground-state $(\text{CO})_2^+$ should have a planar *trans*-configuration with CCO bond angles near 141 degrees. Later theoretical studies [49] are consistent with this structure.

Infrared spectra of Ne:CO = 100 or 200 samples codeposited with a beam of excited neon atoms show a sharp absorption at 2056.6 cm^{-1} which has isotopic substitution behavior appropriate for a species of formula OCCO. Although the high frequency stretching absorptions of O_4^+ and N_4^+ are intermediate between the ground-state stretching fundamentals of the corresponding diatomic neutral and cation species, this absorption lies below the vibrational fundamentals of both CO and CO^+ . Such behavior would be consistent with some enhancement in the strength of the central C \cdots C bond compared to the strength of the N \cdots N bond of N_4^+ , 23 kcal/mol [42].

Although the electron affinity of CO has been reported to be near 1.37 eV [51], CO^- has not been directly detected in either the present infrared or the earlier ESR studies.

In a study of the reaction of alkali metals with CO in an argon matrix, Manceron and co-workers [52] assigned absorptions at 1305 and 1509 cm^{-1} to NaC_2O_2 . Carbon-13 substitution data were given in support of this assignment. When a Ne:CO = 100 or 200 sample was codeposited with a beam of excited neon atoms, prominent, broad absorptions appeared at 1516.4 and 1517.7 cm^{-1} . These absorptions showed carbon-13 and oxygen-18 isotopic substitution behavior appropriate for their assignment to the CO antisymmetric stretching fundamental of a species of formula OCCO. The proximity of this pair of absorptions to the 1509 cm^{-1} peak

previously assigned to the CO antisymmetric stretching fundamental of $\text{Na}^+\text{C}_2\text{O}_2^-$ strongly indicates that the carrier of the neon-matrix absorptions is $(\text{CO})_2^-$. As was proposed in the argon-matrix work, it is likely that the absorption at 1305 cm^{-1} , not seen in the neon-matrix studies, becomes infrared-active because of the asymmetry introduced by the sodium cation.

The absorptions near 1517 cm^{-1} diminished in intensity even on exposure of the sample to radiation of wavelength longer than 560 nm and were readily destroyed when the sample was exposed to radiation of wavelength longer than 490 nm. The peak at 2056.6 cm^{-1} diminished in intensity on irradiation of the sample by visible light until the peaks near 1517 cm^{-1} were destroyed. When the previously identified [53] 1241.6 cm^{-1} absorption of NO_2^- , a particularly stable anion, was also present, residual absorption at 2056 cm^{-1} persisted even when the deposit was exposed to filtered mercury-arc radiation of wavelength longer than 345 or 300 nm. This behavior is consistent with the hypothesis that $(\text{CO})_2^+$, with an absorption at 2056 cm^{-1} , is destroyed by capture of electrons which are photodetached from $(\text{CO})_2^-$, which absorbs infrared radiation near 1517 cm^{-1} . When this source of electrons is exhausted, $(\text{CO})_2^+$ is photolytically stable into the near ultraviolet, as has been reported [54] for gas-phase $(\text{CO})_2^+$.

XIII. CONCLUSIONS

Studies of the molecular spectra of small polyatomic molecular ions are still in their infancy. The availability of survey spectra would facilitate the search for individual vibrational and vibronic bands of gas-phase ion species using sophisticated, highly sensitive laser techniques. Detectable concentrations not only of simple ions such as CO_2^+ and H_2^+ but also of dimer cations and anions such as O_4^+ and O_4^- have been stabilized in solid neon when the parent molecule is codeposited with a beam of excited neon atoms. The vibrational fundamentals heretofore observed for the simple ions isolated in solid neon lie very close to the positions of the corresponding gas-phase band centers. Molecular spectroscopic data are not yet available for the gas-phase dimer ions. Therefore, it is difficult to estimate how closely the neon-matrix vibrational frequencies here reported for a number of dimer ions correspond to the gas-phase band centers. Some guidance is available from comparison of the argon-matrix spectra of small molecules hydrogen-bonded to HF with the gas-phase spectra of these hydrogen-bonded species [55]. In these studies, the effect of the argon matrix is to enhance the apparent hydrogen-bond

strength; the HF stretching frequency is lowered by 1 to 5% from the gas-phase value, and the absorptions contributed by the flexing of the HF with respect to the other molecule are raised by 5% or more. Since neon matrices are generally less perturbing than argon matrices, the deviation from the gas-phase frequencies should be somewhat less in neon-matrix studies. In the present experiments, only the high frequency stretching fundamentals have been observed, suggesting that matrix shifts should amount to less than 3 or 4%. Therefore, matrix isolation studies such as these promise to provide a valuable new tool for the detection and spectroscopic characterization of small molecular ions and cluster ions.

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